Supplementary Information

A Mn(II) coordination framework incorporating the redox-active tris(4-(pyridin-4yl)phenyl)amine ligand (NPy₃): Electrochemical and spectral properties

Carol Hua and Deanna M. D'Alessandro*

School of Chemistry, The University of Sydney, New South Wales 2006, Australia. Fax: +61 (2) 9351 3329; Tel: +61 (2) 9351 3777; E-mail: <u>deanna.dalessandro@sydney.edu.au</u>

Experimental Details

Distilled and degassed acetonitrile (dried over CaH_2) was used for all electrochemical experiments. DMF was dried over activated $CaSO_4$ then distilled under reduced pressure. Microanalyses were carried out at the Chemical Analysis Facility – Elemental Analysis Service in the Department of Chemistry and Biomolecular Science at Macquarie University, Australia.

Synthesis of the [Mn(NPy₃)Cl.3MeOH.DMF]_n framework

The NPy₃ ligand (95.9 mg, 2.01 x 10^{-4} mol) and MnCl₂·4H₂O (198 mg, 1.00 x 10^{-3} mol) were dissolved in distilled DMF (5.0 mL) and methanol (5.0 mL) in a 20 mL vial and heated at 45 °C for 1 day in a heating block. The product, [Mn(NPy₃)Cl·3MeOH·DMF]_n, was obtained as prismatic yellow crystals (138 mg, 79 %).

The framework can be obtained in 30 minutes on a smaller scale using 20 mg of ligand under the same reaction conditions in a 2 mL vial.

UV-Vis-NIR (solid state): 19850, 22570, 29210, 39640 cm⁻¹.

As synthesised: Found C, 63.74; H, 5.56 and N, 9.44; Calculated for $C_{33}H_{24}ClMnN_4 \cdot 3MeOH \cdot DMF$: C, 63.63; H, 5.89 and N, 9.51%

Oxidation of the [Mn(NPy₃)Cl.3MeOH.DMF]_n framework

<u>Br</u>₂: A 2 mL vial containing the $[Mn(NPy_3)Cl \cdot 3MeOH \cdot DMF]_n$ framework was placed in a beaker containing 3 drops of bromine with a watchglass placed on top. The bromine vapour was then allowed to diffuse into the framework material over 30 minutes.

<u>NOBF</u>₄: The $[Mn(NPy_3)Cl \cdot 3MeOH \cdot DMF]_n$ framework was suspended in dry and distilled acetonitrile (2 mL) and the mixture thoroughly degassed. A solution of nitrosium tetrafluoroborate (10 mg, 0.0860 mmol) in acetonitrile (2 mL) was added slowly dropwise. Over the course of 5 minutes, the framework was observed to dissolve to form a bright yellow solution.

 $\underline{Cu(OTf)_2}$: A saturated solution of copper(II) triflate in water was added to the framework with no observable change.

<u>I</u>₂: Iodine vapour was allowed to diffuse into the $[Mn(NPy_3)Cl\cdot 3MeOH \cdot DMF]_n$ framework overnight yielding a colour change from yellow to orange-brown.

<u>Ce(IV)</u>: A solution of ammonium cerium nitrate in water was added to a suspension of the $[Mn(NPy_3)Cl\cdot 3MeOH \cdot DMF]_n$ framework in water. A colour change from yellow to red was observed.

Crystallography

<u>X-ray single crystal structure of $[Mn(NPy_3)Cl\cdot 3MeOH\cdot DMF]_n</u>: A single crystal of <math>[Mn(NPy_3)Cl\cdot 3MeOH\cdot DMF]_n$ was coated in a thin film of paratone-*N* oil and mounted on a mohair fibre affixed to a goniometer head. The crystal was quenched in a cold nitrogen gas stream from an Oxford Cryosystems Cryostream. An Oxford Supernova diffractometer with Cu-K α radiation ($\lambda = 1.5418$ Å) at 150 K was used for the data collection. The data integration and reduction were performed using the Agilent Technologies CrysAlisPro software (version 1.171.35.8).^[1] Empirical absorption corrections were made using SCALE3 ABSPACK2.^[1] The structure was solved in the space group *Pbcn* by direct methods using SHELXS-97^[2] and refined using SHELXL-97^[3] in WinGX.^[4] The SQUEEZE function in PLATON was used to treat the disordered solvent molecules present in the pores of the framework.^[5]</u>

The asymmetric unit contains the unique unit of the framework and methanol solvent molecules. The non-hydrogen atoms in the asymmetric unit were modelled with anisotropic displacement parameters and a riding atom model with group displacement parameters was used for the hydrogen atoms. Guest-accessible pore volumes were calculated in PLATON.^[5]

Parameter	
Formula	$C_{33}H_{24}ClMn_{0.5}N_{4}$
M/g mol ⁻¹	539.48
Temperature (K)	150(2)
Crystal system	orthorhomic
Crystal size (mm ³)	$0.25 \times 0.12 \times 0.11$
a (Å)	28.7320 (1)
b (Å)	13.5996 (1)
c (Å)	17.5750 (1)
V (Å ³)	6867.32 (7)
Z	8
$\rho_{calc} (mg/mm^3)$	1.044
$\mu (mm^{-1})$	1.478
Reflections collected	170380/6772[R(int) = 0.034]
R1(F)	0.0346
$wR2(F^2)$	0.0941
Goodness-of-fit on F^2	1.042

Table S1. Crystal data and structure refinement details for $[Mn(NPy_3)Cl \cdot 3MeOH \cdot DMF]_n$

 $RI = \Sigma(|F_o| - |F_c|) / \Sigma(|F_o|); wR_2 = [\Sigma\{w(F_o^2 - F_c^2)^2\} / \Sigma\{w(F_o^2)^2\}]^{1/2}$

Physical Characterisation

General details: Thermal gravimetric analysis was performed under a flow of nitrogen (0.1 L/min) on a TA Instruments Hi-Res Thermogravimetric Analyser from 25-600 °C at 1 °C/min. Powder X-ray diffraction (PXRD) data were obtained on a PANalytical X'Pert PRO Diffractometer producing Cu α (1.5406 Å) radiation, where the sample was lightly ground prior to analysis.

UV/Vis/NIR: UV/Vis/NIR spectroscopy was performed on a Cary 5000 Spectrophotometer equipped with a Harrick Praying Mantis accessory, where dried KBr was used for the baseline. Spectra are reported as the Kubelka-Munk transform, where $F(R) = (1-R)^2/2R$ (*R* is the diffuse reflectance of the sample as compared to KBr).

Solid State Electrochemistry: Solid state electrochemical measurements were performed using a Bioanalytical Systems Epsilon Electrochemical Analyser. Argon was bubbled through solutions of 0.1 M [$(n-C_4H_9)_4N$]PF₆ dissolved in distilled CH₃CN. The cyclic voltammograms (CVs) were recorded using a glassy carbon working electrode (1.5 mm diameter), a platinum wire auxiliary electrode and an Ag/Ag⁺ wire quasi-reference electrode. Solid state samples were mounted on the

glassy carbon working electrode by dipping the electrode into a paste made of the powder sample in acetonitrile. Ferrocene was added as an internal standard upon completion of each experiment. All potentials are quoted in mV versus Fc/Fc^+ .

Solid State Spectroelectrochemistry: The diffuse reflectance spectra of the electrogenerated species were collected *in situ* in a 0.1 M $[(n-C_4H_9)_4N]PF_6/CH_3CN$ electrolyte over the range 5000-25000 cm⁻¹ using a Harrick Omni Diff Probe attachment and a custom built solid state spectroelectrochemical cell described previously.^[6] The cell consisted of a Pt wire counter electrode and Ag/Ag⁺ quasi reference electrode were used. The solid sample was lightly ground then immobilised onto an 0.1 mm thick Indium-Tin-Oxide (ITO) coated quartz slide (which acts as the working electrode) using a thin strip of Teflon tape. The applied potential (from 0.5 V to 3.0 V) was controlled using an eDAQ potentiostat. Continuous scans of the sample were obtained and the potential increased gradually until changes in the spectrum were observed.

Fluorescence: Fluorescence spectra were performed on a Varian Cary Eclipse Fluorescence spectrophotometer in the solid state. The scan rate used for all measurements was 120 nm/min with a 1 nm data interval. The fluorescence spectrum of the framework in the solid state was performed by gently pressing a thin film of the dry powder using a spatula onto a quartz plate resting diagonally inside a 1 cm x 1 cm quartz cuvette. The excitation beam was aligned with light at 550 nm with each measurement to ensure that the solid sample was being irradiated. The sample was excited at 400 nm, the emission spectrum obtained from 410-750 nm and 2.5 mm slit widths were used for both excitation and emission. The cuvette and quartz slide were washed with concentrated nitric acid, water and acetone prior to use.

Figures



Figure S1: Thermal gravimetric analysis (TGA) of $[Mn(NPy_3)Cl \cdot 3MeOH \cdot DMF]_n$ over the range 25-600 °C



Figure S2: PXRD of the synthesised framework ('scaled up') versus the predicted pattern from the crystal structure.



Figure S3: PXRD of the oxidised framework with bromine and iodine as the oxidants versus the neutral framework



Figure S4: Infrared spectrum of $[Mn(NPy_3)Cl \cdot 3MeOH \cdot DMF]_n$ over the range 500-4000 cm⁻¹



Figure S5: Fluorescence spectrum plotted against the absorption spectrum of $[Mn(NPy_3)Cl\cdot 3MeOH \cdot DMF]_n$ over the range 400-750 nm

References

- 1 CrysAlisPro, Yarnton, Oxfordshire. OX5 1QU, UK.
- 2 G. M. Sheldrick, *SHELX97 programs for crystal structure analysis*, University of Göttingen. Institüt für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.
- 3 G. M. Sheldrick, *SHELXTL reference manual: Version 5*, Analytical X-ray Instruments Inc., Madison, Wisconsin, USA, 1996.
- 4 L. Farrugia, *Journal of Applied Crystallography* 1999, **32**, 837-838.
- 5 A. L. Spek, *Journal of Applied Crystallography* 2003, **36**, 7.
- 6 P. M. Usov, C. Fabian, D. M. D'Alessandro, *Chemical Communications* 2012, **48**, 3945-3947.